

# PATENT SPECIFICATION

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## (54) METHOD FOR PRODUCING BIAXIALLY STRETCHED ORIENTED TUBULAR FILMS OF VINYLIDENE CHLORIDE

(71) We, KUREHA KAGAKU KOGYO KABUSHIKI KAISHA, a Japanese Joint-Stock Company, of 8, 1-Chome, Nihonbashi Horidome-Cho, Chuo-Ku, Tokyo-To, Japan, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to a method for producing vinylidene chloride tubular films.

Crystalline vinylidene chloride copolymers are resins of extremely low hygroscopicity and gas permeability, and have been widely used as food-packaging material. However, as their low-temperature characteristic is inferior, i.e., the resins are poor in their impact resistance at a low temperature, improvement therein has so far been made by increasing the quantity of a plasticizer added to the resins. In this case, when the quantity of the plasticizer greatly exceeds the amount which will dissolve in the resin (usually about 20%, or less, depending on the composition of the polymer), the plasticizer tends to migrate rapidly, or it becomes easily extracted by organic solvents, which makes the resin unfavourable as a film material for food-packaging purposes. In order therefore to eliminate this deficiency, it has been proposed to add a rubbery or elastic substance to the resin prior to extrusion thereof. However, when crystalline vinylidene chloride copolymer resin is mixed with an elastic substance, for example cross-linked rubber, having a high modulus of elasticity, the modulus of elasticity of the mixture greatly increases, thus causing inferior molecular orientation, due to stretching, of the crystalline vinylidene chloride copolymer resin. Alternatively, when an easily fluidizing rubbery substance is used, the mixture is amorphous even after shaping, with the result that the composition remains fluid even after cooling. In either case mentioned above, creeping readily occurs due, in the case of the former, to the inferior mole-

cular orientation and the amorphous portion of the crystalline vinylidene chloride copolymer remaining in a state whereby it can be easily fluidized and deformed, and, in the case of the latter, to the rubbery substance still being fluid.

The resin compositions prepared in the above two instances are not particularly suitable as food packaging film, because the film material is not only deformed at the time of pressure-filling of kneaded products for example sausage, into casing made of the film (or readily loses its thermal stress at the time of high temperature heating with the consequent slackening of the film to spoil the outer appearance of the food package, when the content in the casing shrinks due to cooling), but also, in the case of meat packaging, gravy separates and collects between the film and the meat thus causing accelerated putrefaction.

It is therefore an aim of the invention to provide a method for producing vinylidene chloride films of improved quality which are entirely free from the aforementioned defects and are suitable for food packaging purposes.

It is another aim of the present invention to provide a method for producing vinylidene chloride films whose crystallographic orientation is highly improved.

According to the invention, there is provided a method for producing biaxially oriented tubular films of vinylidene chloride which comprises:

- a. preparing a resin composition consisting of 100 parts by weight of crystalline vinylidene chloride copolymer composed of 60% to 95% by weight of vinylidene chloride and 40% to 5% by weight of a vinyl-containing monomer containing vinyl chloride as its principal component, 1 to 20 parts by weight of a plasticizer, 0.3 to 10 parts by weight of a stabilizer and 2 to 30 parts by weight of a synthetic elastomeric substance compatible with the vinylidene chloride copolymer;

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Four vinylidene chloride/vinyl chloride copolymer resins were prepared with the following compositions (ratios and parts by weight).

(I) Copolymer of vinylidene chloride and vinyl chloride (80:20)			100 parts
Plasticizer (dibutyl sebacate ("DBS"))			7 "
Stabilizer (epoxidized soy bean oil)			2 "
Synthetic Elastomeric substance (ethylene/vinyl acetate/ethyl acrylate copolymer - 68:23:9)			10 "
(II) Copolymer of vinylidene chloride and vinyl chloride (80:20)			100 parts
Plasticizer (dibutyl sebacate "DBS")			7 "
Stabilizer (epoxidized soy bean oil)			2 "
Synthetic Elastomeric material (ethylene/vinyl acetate copolymer - 67:33)			10 "
(III) Copolymer of vinylidene chloride and vinyl chloride (80:20)			100 parts
Plasticizer (dibutyl sebacate "DBS")			7 "
Stabilizer (epoxidized soy bean oil)			2 "
Synthetic Elastomeric material (a substance prepared by post-polymerization of SBR (styrene butadiene rubber) consisting of 100 parts by weight of butadiene/styrene copolymer (80:20) on 25 parts by weight of a component consisting of styrene/methylmethacrylate copolymer (10:15) )			20 parts
(IV) Copolymer of vinylidene chloride and vinyl chloride (80:20)			100 parts
Plasticizer (dibutyl sebacate "DBS")			7 "
Stabilizer (epoxidized soy bean oil)			2 "
Synthetic Elastomeric material			none

Each of the above resins was melt-extruded as a tubular film by a conventional method, and then quenched by water at 10°C.

5 The resins (I) to (III) were then inflation-moulded by fitting a cylindrical heating

apparatus at a portion where the film is subjected to orientation and inflation-moulding (i.e., the neck portion), and heating this portion for 3 seconds at temperatures specified in the following Table.

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- b. melt-extruding the resin composition as a tubular film followed by rapid cooling; and
- 5 c. continuously inflating the film, while strongly heating the same at a neck portion of the film at a temperature ranging from a temperature at which the tubular film commences softening to a temperature not exceeding 300°C for a period of from 1 to 7 seconds.
- 10 2. A method as claimed in claim 1, in which the synthetic elastomeric substance is one selected from the group consisting of copolymers of ethylene/vinyl acetate, ethylene/vinyl acetate/ethyl acrylate, and a composition prepared by post-polymerization of a substance
- 15 consisting of 100 parts by weight of butadiene/styrene copolymer on 25 parts by weight of a substance consisting of styrene/methylmethacrylate copolymer.
3. A method for producing biaxially oriented films of vinylidene chloride copolymers as claimed in claim 1 and as described hereinbefore with reference to the Examples. 20

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